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Hydrogen Bonding in Complex Salts of $[Fe(CN)_6]^{3-}$ with Ammine Derivatives of Co(III) and Cr(III)

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The study of the IR spectra and conductivity measurements in different solvents of salts of the anion $[Fe(CN)_6]^{3-}$ *with the cations* $[Co(H_2O)(NH_3)_5]^{3+}$, $[Co(H_2O)_2(NH_3)_4]^{3+}$, $[Cr(H_2O)(NH_3)_5]^{3+}$ *and* $[Cr(H_2O)_2(NH_3)_4]^{3+}$ *have shown the occurrence of strong interionic hydrogen bonds.*

Introduction

In a previous communication [1], we described the preparation and study of the compounds $[CrH_2O(NH_3)_5][Fe(CN)_6]$ and $[Cr(H_2O)_2(NH_3)_4][Fe(CN)_6]$. The compounds exhibited splitting of the CN stretching band and were identified as dinuclear compounds with μ-cyano ligand. Further study on these and the analogous compounds of Co(III), $[CoH_2O(NH_3)_5][Fe(CN)_6]$ [2] and $[Co(H_2O)_2(NH_3)_4][Fe(CN)_6]$ have shown that they cannot be considered as dinuclear compounds but as ionic compounds with strong hydrogen bond interactions between anion and cation.

The four salts mentioned are isomorphous as shown by the diffraction patterns [3] and in agreement with the isomorphism previously reported by several authors [2, 4] for salts of the type $[Co(NH_3)_6][M(CN)_6]$, $[Cr(NH_3)_6][M(CN)_6]$ (where no formulation as dinuclear complexes with μ-cyano bridge is possible), $[Co(H_2O)(NH_3)_5][M(CN)_6]$ [M = Co(III), Cr(III), Fe(III), Mn(III)], and $[Co(H_2O)_2(NH_3)_4][Co(CN)_6]$ [5].

On the other hand, several dinuclear compounds with ligand μ-cyano have been prepared from $[CoH_2O(NH_3)_5][Co(CN)_6]$ and $[Co(H_2O)_2(NH_3)_4][Co(CN)_6]$ by prolonged heating for long periods in the solid state [6–8]. The authors have also prepared and characterized several dinuclear complexes of the same class, from analogous complex salts [9].

A new study of the four salts of $[Fe(CN)_6]^{3-}$ has led us to show the existence of strong interactions attributable to interionic hydrogen bonding. Such interactions have been shown to occur by IR spectroscopy and conductivity measurements in solvents of lower polarity than water (DMF, $\epsilon = 36$; DMSO, $\epsilon = 45$) or mixtures of these and water.

Experimental

Preparative and Analytical Methods

$[CrH_2O(NH_3)_5][Fe(CN)_6]$ and $[Cr(H_2O)_2(NH_3)_4][Fe(CN)_6]$ were prepared as already described by us [1]; $[CoH_2O(NH_3)_5][Fe(CN)_6]$ was prepared as reported in the literature [2]; the new compound $[Co(H_2O)_2(NH_3)_4][Fe(CN)_6]$ was prepared by direct synthesis from $[Co(H_2O)_2(NH_3)_4](ClO_4)_3$, $Na_3[Fe(CN)_6]$ and acetic acid.

The usual analytical methods for Co(III), Cr(III), NH_3 and $[Fe(CN)_6]^{3-}$ [10] gave results in good agreement with the proposed formulae.

IR Spectra and Conductivity Measurements

IR spectra were obtained on a Beckman IR 20A infrared spectrophotometer. Samples were prepared using the KBr disk technique. Conductivity measurements were obtained with a Radiometer CDM-3 conductivity bridge. The following solvents at dilution 10^{-3}–10^{-4} *M* were used: water, DMF, DMSO and mixtures of water and DMSO at different proportions.

Results and Discussion

Infrared Spectra

Fig. 1 shows a typical IR spectrum of the salts studied, in the 4000–2000 cm^{-1} range. The bands appearing at 3450–3400 cm^{-1} and 3300–3250 cm^{-1} are attributed to O–H and N–H stretching of coordinated H_2O and NH_3 respectively [11]. Further, all of the salts studied in this work exhibit a very strong band centered at 3100 cm^{-1} which does not appear

TABLE I. Infrared spectra: NH_3 rocking band.

Species	Wavenumber (cm^{-1})		Species
$[CrH_2O(NH_3)_5](ClO_4)_3$	750–755	775	$[CrH_2O(NH_3)_5][Fe(CN)_6]$
$[Cr(H_2O)_2(NH_3)_4](ClO_4)_3$	750–755	775	$[Cr(H_2O)_2(NH_3)_4][Fe(CN)_6]$
$[CoH_2O(NH_3)_5](ClO_4)_3$	820–825	855	$[CoH_2O(NH_3)_5][Fe(CN)_6]$
$[Co(H_2O)_2(NH_3)_4](ClO_4)_3$	820–825	860	$[Co(H_2O)_2(NH_3)_4][Fe(CN)_6]$

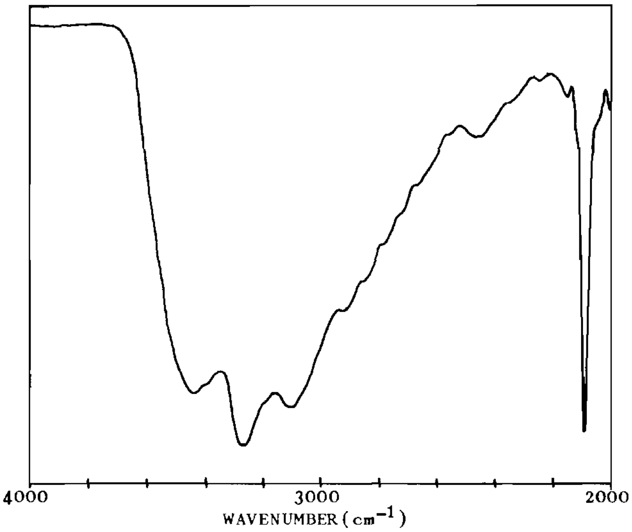

Figure 1. Infrared Spectra of $[CoH_2O(NH_3)_5][Fe(CN)_6]$ or $[Co(H_2O)_2(NH_3)_4][Fe(CN)_6]$.

in most of the ammine complexes of Cr(III) and Co(III) thus far reported by us [12–16]. The band may be attributed to the formation of hydrogen bonding of the type OH----N (with both coordinated H_2O and CN) in agreement with the results obtained by Nakamoto [17] and Novak [18] on organic and inorganic compounds with the same type of interaction. According to these authors, the OH----N interaction is evidenced by a broad and strong band in the 3120–3190 cm^{-1}.

A group of broad, weak and poorly-defined bands (see Fig. 1) occurs in the 2400–3000 cm^{-1} range, which may be attributed to the presence of hydrogen bonds of the type NH----N in agreement with the observations of Novak [18] on a number of organic compounds showing such interaction (imidazole, triazole, *etc.*). The anharmonicity of the ν(NH) vibration is the factor responsible for the type and broadness of the bands; and the large number of bands observed (some of them partially overlapping with one another) is due to Fermi resonance among the fundamental vibration ν(N–H) and the overtones and combination bands of the antisymmetric degenerate vibration of coordinated NH_3.

This occurrence of the new bands has also been observed by Curtis [19] in the complexe $[Ni(teta)(CN)_2]$ where two CN groups occur held together by hydrogen bonding [teta = hexamethyltetraazacyclotetradecane].

The best-defined band (in this 3000–2200 cm^{-1} range) appears around 2450–2500 cm^{-1} (see Fig. 1). Doadrio *et al.* [20–23] in a study of more than 50 salts of the anions $[PdCl_4]^{2-}$ and $[AuCl_3]^-$ with organic amines, proved the existence of hydrogen bond interactions between anion and cation by the presence of a broad band in the 2500–2600 cm^{-1} range, attributable to N–H or N–H$^+$ (protonated amine) vibrations which are shifted to lower frequencies due to the formation of hydrogen bonds. The shifts, according to the authors, is a measure of the strength of the hydrogen bond formed. In the four complexes of $[Fe(CN)_6]^{3-}$ this band appears lower than the frequencies observed by Doadrio, which can indicate that the hydrogen bond is stronger.

The band due to the ν(CN) vibration occurs at 2110–2120 cm^{-1}, weakly split at 2175 cm^{-1} for the Co(III) salts (Fig. 1), and at 2140 cm^{-1} for the Cr(III) salts [1]. This splitting is never observed in the ionic hexacyanoferrate(III)(Na$^+$, K$^+$) but it does not correspond, on the other hand, to the intense splitting of a dinuclear complex with μ-cyano ligand [6, 7, 9].

Moreover, all of the salts studied in this work exhibit the NH_3 rocking band displaced to higher frequencies with respect to the salts of $[M(H_2O)(NH_3)_5]^{3+}$ and $[M(H_2O)_2(NH_3)_4]^{3+}$ (Table I) where no strong hydrogen bond interactions are to be expected. The displacement is consistent with the fact, as observed by Nakamoto [11], that such band is most sensitive to the coordination of new ligands (very unlikely here) or to the formation of hydrogen bonds with hydrogen of coordinated NH_3.

The other bands are unaffected by hydrogen bonding: 1610 cm^{-1} (OH bending and NH_3 antisymmetric deformation); 1360–1380 cm^{-1} (NH_3 symmetric deformation); 475 cm^{-1} [ν(Fe–C)] and 380 cm^{-1}

[δ(Fe–CN)] [11, 24]. Therefore, IR spectra show that the hydrogen bonds can occur between the hydrogen atom of H_2O or NH_3 and the nitrogen atom of the cyano group.

Conductivity Measurements

The solubility of the four salts in DMF or DMSO is about 10^{-4} *M*. Molar conductivity in DMF at 25 °C is about 0–6 ohm^{-1} mol^{-1} cm^2 and about 5–10 (in the same units) in DMSO. Therefore the four salts behave as non-electrolytes in these low-polarity solvents [25]. No change of the conductivity with time was observed.

A complete breakdown of the hydrogen bonds occurs on dissolving the salts in water ($\epsilon = 79$) and values of molar conductivity corresponding to two-ion electrolytes are observed ($\Lambda^{20^\circ} = 200$–260 ohm^{-1} mol^{-1} cm^2) [26]. Conductivities are about 20–25 ohm^{-1} mol^{-1} cm^2 in the mixed solvent DMSO:H_2O(70% in DMSO; $\epsilon = 69$); these values are somewhat lower than those found for salts giving two ions in the same mixed solvent [25]. However, the values of Λ^{25° are about 50–60 ohm^{-1} mol^{-1} cm^2 in DMSO:H_2O (50%; $\epsilon = 75{,}2$), consistent with two-ion electrolytes [25].

Conductivity measurements in low polarity solvents give, according to Doadrio [23] and Petrov [27] an approximate idea of the strength of the hydrogen bonds between cations and anions; on the other hand, Curtis [19] found a negligible conductivity for the compound [Ni(teta)$(CN)_2$] in dichloromethane ($\epsilon = 11$) and a weak but noticeable conductivity in methanol ($\epsilon = 34$). In our case, where conductivities are noticeable only in solvents of ϵ greater than 45 and are those expected according to stoichiometry for solvents with ϵ greater than 70, we may state that hydrogen bond interactions may be considered quite strong in these compounds.

The hydrogen bond is believed, on the basis of its strength, not to be localized between a CN group and a NH or OH group but, probably, among several CN groups and the nearest hydrogen atoms.

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